

Spatially Resolved Dynamic Structure Factor of Finite Systems from MD Simulations

Thomas Raitza* and Gerd Röpke†
*Institut für Physik, Universität Rostock,
18051 Rostock, Germany*

Heidi Reinholz‡
*Institut für Theoretische Physik,
Johannes-Kepler- Universität Linz,
4040 Linz, Austria and
Institute of Physics, University of Western Australia,
Perth, 6009 WA, Australia*

Igor Morozov§
*Joint Institute for High Temperatures of RAS,
Izhorskaya, 13, build. 2,
Moscow 125412, Russia
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The dynamical response of metallic clusters up to 10^3 atoms is investigated using a molecular dynamics simulations scheme. Exemplarily, sodium like material is considered. Correlation functions are evaluated to investigate the spatial structure of collective electron excitations and optical response of laser excited clusters. In particular, the spectrum of bi-local correlation functions shows resonances representing different modes of collective excitations inside the nano plasma. The spatial structure, the resonance energy and width of the eigenmodes have been investigated in dependence on electron density, temperature, cluster size and ionization degree. Comparison with bulk properties is performed and the dispersion relation of collective excitations is discussed.

* thomas.raitz@uni-rostock.de

† gerd.roepke@uni-rostock.de

‡ heidi.reinholz@jku.at

§ morozov@ihed.ras.ru

I. INTRODUCTION

Nano plasmas can now be readily produced in laser irradiated clusters, and new physical phenomena have come into focus experimentally as well as theoretically. Interactions between laser fields of $10^{13} - 10^{16} \text{ W cm}^{-2}$ and clusters have been investigated over the last few years, see Refs. [1]–[9]. After laser interaction, extremely large absorption rates of nearly 100% were found in clusters, see [10], as well as X-ray radiation, see Refs. [11]–[17]. In pump-probe experiments by Döppner [9] and Fennel [18] a nano plasma was generated with a first pulse in order to probe it with a second pulse. With the focus on optical properties, we will discuss the dynamical response function of the electrons in a nano plasma. For example, the absorption rate of a second laser pulse is closely connected with the dynamical behavior.

Collective electronic excitations of the nano plasma are interpreted as Mie resonances of a homogeneously charged sphere. Absorption cross section experiments by Kresin *et al.* [19] show multiple resonance structures indeed. The effect of collective electron motion can also be seen in ultraviolet (UPS) and x-ray photoelectron spectroscopy (XPS) experiments, see [20], which are used to detect binding energies of core level electrons in small metal clusters [21, 22]. In fusion related experiments by Ditmire *et al.* [23], Grillon *et al.* [24], as well as Madison *et al.* [25] ignition processes are started via irradiation of deuterium clusters. Collective effects in the optical response are discussed in the context of metallic nanoshells by Höflich *et al.* [26] as well as nanocavities by Maier *et al.* [27].

In theoretical calculations of finite systems, see Raitza *et al.* [28–31], a more complex resonance structure was found. Earlier investigations by Reinhard *et al.* [32] and Kull *et al.* [33, 34] led to comparable results. The method of resonance structure analysis using spherical harmonics is known from the discussion of giant dipole resonances of nuclei by Reinhard *et al.*, in [35]. Quantum and semi-classical methods, see Refs. [36]–[38], respectively, were used to investigate the cluster excitation via laser fields. Collisional absorption processes in nano plasmas have been the subject of theoretical investigations in [39]. Using density functional theory (DFT) calculations, the electronic structures of cold clusters were analyzed by Ekardt [40], Kümmel *et al.* [41], Brack *et al.* [42], as well as Krotscheck *et al.* [43]. The damping of collective electron oscillations was investigated by Ramunno *et al.* [44] emphasizing the importance of collisional processes beside the Landau damping.

In this work, molecular dynamics (MD) simulations will be used to study nano plasmas in metal clusters. Clusters consisting of 55 up to 1000 sodium like atoms are considered after laser irradiation with intensities in the order of $10^{12} \text{ W cm}^{-2}$. Properties of the nano plasma are mainly determined by the dynamics of electrons which are bound to the cluster but ionized from the former atoms, comparable to conduction electrons in bulk systems. As already shown in earlier publications, see [28], plasma parameters as known from bulk (temperature and particle density) but also the cluster size and net charge are justified for characterization since the electrons can be assumed to be in local thermal equilibrium within time scales considered here. We focus on parameter ranges where the plasma can be treated classically. Strong correlations are taken into account via collisions of all particles. Concepts that have been well established for infinite bulk systems near thermodynamic equilibrium have to be modified for applications to finite systems, e.g. clusters. In particular, we are interested in the dynamical structure factor and the response function for such finite nano plasmas. In order to bridge from finite systems to bulk plasmas, we investigate size effects, e.g. in the dynamical collision frequency. First results in this direction have been reported in Refs. [28, 45, 46].

In Sec. II, correlation functions and their relation to optical properties of homogeneous bulk plasma are introduced as far as it will be of interest to extend the approach to finite systems. Expressions will also be used for comparison with nano plasmas in the limit of large clusters. Sec. III explains the *restricted* MD scheme for the calculation of the particle trajectories from which the total and bi-local current density correlation functions are determined. Symmetries in the correlation matrix as discussed in Sec. IV can be used for an improved statistics. The decomposition of the correlation matrix into eigenvectors and eigenvalues is interpreted as a decomposition into collective excitation modes. In Sec. V, the excitation modes will be characterized with respect to spherical harmonics. In the further analysis, we focus on modes with a dipole moment, which are also seen in the total current density auto-correlation function. First results for resonance frequencies and damping are presented. Regarding the dipole-like modes, the spatial structure at the selected resonance frequency will be discussed in Subsec. A and Subsec. B. Conclusion and outlook are given in Sec. VI.

II. THEORY OF THE LINEAR RESPONSE OF PLASMAS IN EQUILIBRIUM

Within linear response theory as derived by Kubo *et al.*, see [47], the reaction of a many-particle system to weak external perturbations can be related to the dynamical behavior of fluctuations in thermal equilibrium. Denoting the equilibrium statistical operator with ρ_0 , we introduce the two-time correlation function of the fluctuations $\delta A_i(t) =$

$A_i(t) - \text{Tr}\{A_i\rho_0\}$ as the Kubo scalar product

$$(A_i(t); A_j(0)) = \beta \int_0^1 d\lambda \text{Tr}\{\delta A_i(t) \delta A_j(i\hbar\beta\lambda)\rho_0\}, \quad (1)$$

where the time dependence is given in the Heisenberg picture. The indices i and j identify quantum observables. In particular we consider local properties so that they contain also the position $\vec{r}$. In case of $i = j$, it is called an auto-correlation function.

In the classical case, equilibrium two-time correlation functions can be calculated according to

$$(A_i(\vec{r}, t); A_j(\vec{r}', 0)) = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T d\tau \delta A_i(\vec{r}, \tau + t) \cdot \delta A_j(\vec{r}', \tau), \quad (2)$$

where we assumed ergodic systems - the ensemble average can be replaced by a time average. The spectrum of the equilibrium correlation function $\langle A_i(\vec{r}); A_j(\vec{r}') \rangle_\omega$ then results from Laplace transformation.

We consider an, induced electron density fluctuation $\delta n_e(\vec{r}, t) = n_e(\vec{r}, t) - n_{e,0}(\vec{r})$ at time t as the deviation from the equilibrium density distribution $n_{e,0}(\vec{r})$ due to an external potential $U_{\text{ext}}(\vec{r}', t')$ at time $t' < t$, which is only dependent on the time difference $\Delta t = t - t'$ and one is able to discuss its spectrum after Laplace transform. In the same way, the induced electric current density $\vec{j}_e(\vec{r}, t)$ is related to the external electric field $\vec{E}(\vec{r}', t')$. Via Kubo's theory these induced quantities, $\delta \langle n_e(\vec{r}) \rangle_\omega$ and $\delta \langle \vec{j}(\vec{r}) \rangle_\omega$, can be expressed within linear response, see [47], p. 35, as

$$\delta \langle n_e(\vec{r}) \rangle_\omega = \beta \int d^3\vec{r}' \langle \delta n_e(\vec{r}); \delta \dot{n}_e(\vec{r}') \rangle_\omega U_{\text{ext}}(\vec{r}', \omega), \quad (3)$$

$$\delta \langle \vec{j}(\vec{r}) \rangle_\omega = \beta \int d^3\vec{r}' \langle \vec{j}(\vec{r}); \vec{j}(\vec{r}') \rangle_\omega \vec{E}(\vec{r}', \omega). \quad (4)$$

The spectrum of the density fluctuation correlation $\langle \delta n_e(\vec{r}); \delta \dot{n}_e(\vec{r}') \rangle_\omega$ is related to the scalar response function. The current density correlation $\langle \vec{j}(\vec{r}); \vec{j}(\vec{r}') \rangle_\omega$ represents in general a tensor due to the directions of the current density vector. The material properties of homogeneous bulk plasmas with electron density n_e and inverse temperature β are only dependent on the difference of the positions $\Delta\vec{r} = \vec{r} - \vec{r}'$. Thus, after Laplace transform of the spatial difference $\Delta\vec{r}$, the correlations are dependent on a wave vector $\vec{k}$.

The optical response of a homogeneous bulk plasma will be found, i.e. discussing the dynamical structure factor, which is directly related to the density fluctuation correlation, as

$$S(\vec{k}, \omega) = \frac{1}{2\pi N} \langle \delta n_k; \delta n_k \rangle_\omega. \quad (5)$$

Going from density fluctuation to current density correlation function, the dynamical structure factor can be divided into a static part $S_0(\vec{k})$ and a dynamical part which is directly related to the longitudinal part of the current density correlation function

$$S(\vec{k}, \omega) = \frac{S_0(\vec{k})}{-i\omega} + \frac{1}{2\pi N} \frac{k^2}{\omega^2} \langle \vec{j}_k^{\parallel}; \vec{j}_k^{\parallel} \rangle_\omega. \quad (6)$$

It is of fundamental interest to describe the collective behavior of the system as response to external fields, in particular emission, absorption and scattering of light. In bulk systems, the wave vector and frequency dependent response function reads

$$\chi(\vec{k}, \omega) = -i\beta\Omega_0 \frac{k^2}{\omega} \langle \vec{j}_k^{\parallel}; \vec{j}_k^{\parallel} \rangle_\omega, \quad (7)$$

which can be evaluated using quantum statistical approaches such as Green function theory, see [48], or numerical approaches such as MD simulations, see [50]. In the long wavelength limit ($k \rightarrow 0$), the dynamical collision frequency $\nu(\omega)$ is related to the generalized Drude formula, see [49]

$$\lim_{k \rightarrow 0} \chi(\vec{k}, \omega) = \frac{\varepsilon_0 k^2 \omega_{\text{pl}}^2}{(\omega^2 - \omega_{\text{pl}}^2) + i\omega\nu(\omega)}, \quad (8)$$

with the plasmon frequency $\omega_{\text{pl}} = [n_e e^2 / (m_e \epsilon_0)]^{1/2}$. In the classical case the current density correlation function has been extensively discussed including the long wavelength limit $k \rightarrow 0$ applying MD simulations and perturbative approaches. Exemplarily, one can refer to [50].

The state of a homogeneous one-component plasma in thermodynamic equilibrium is characterized by the non-ideality parameter $\Gamma = e^2(4\pi n_e/3)^{1/3}(4\pi\epsilon_0 k_B T_e)^{-1}$ and the degeneracy parameter $\Theta = 2m_e k_B T_e \hbar^{-2} (3\pi^2 n_e)^{-2/3}$. Considering the response function $\chi(\vec{k}, \omega)$ in the long wavelength limit, a sharp peak arises at the plasmon frequency ω_{pl} . For finite wavelengths the resonance is shifted and can be approximated by the so called Gross-Bohm plasmon dispersion for small wave numbers k , see [51, 52], $\omega(k) \approx \omega_{\text{pl}} + 3k^2/\kappa^2 + \dots$ with the Debye screening length $\kappa^{-1} = [n_e e^2 / (\epsilon_0 k_B T_e)]^{-1/2}$. This relation has recently been revisited by [53] with respect to the relevance of collisions. The general behavior of the response function $\chi(\vec{k}, \omega)$ in the long wavelength limit can be understood with the help of the dynamical collision frequency, using Eq.(8), see [53] and [54]. In the two-component plasma, a phonon mode can arise in addition to the plasmon excitations.

The response function $\chi(\vec{k}, \omega)$ and the related dynamical structure factor $S(\vec{k}, \omega)$ as well as the optical properties have been intensively investigated for electron-ion bulk systems, see [53] and [55], and will not be further reported here. In this work, the inhomogeneous case of finite clusters in local thermal equilibrium will be discussed. The response of inhomogeneous systems is not only dependent on the difference of the positions, but on $\vec{r}$ and $\vec{r}'$ separately. Therefore, the bi-local current density correlation function $\langle \vec{j}(\vec{r}); \vec{j}(\vec{r}') \rangle_\omega$ can not be diagonalized by spatial Fourier transform. Instead of plane waves, other mode functions will be found below to describe the collective excitation of electrons.

III. MD SIMULATIONS OF FINITE PLASMAS

Finite plasma systems have been investigated using the restricted molecular dynamics (RMD) simulations based on a MD scheme by Suraud *et al.* [56]. A two-component system of singly charged ions and electrons will be described using an error function pseudo potential for the interaction of particles i and j

$$V_{\text{erf}}(r_{ij}) = \frac{Z_i Z_j e^2}{4\pi\epsilon_0 r_{ij}} \text{erf}\left(\frac{r_{ij}}{\lambda}\right), \quad (9)$$

where Z_i is the charge of the i th particle. The Coulomb interaction is modified at short distances, assuming a Gaussian electron distribution that takes quantum effects into account. Considering a sodium like system, the potential parameter $\lambda = 0.318$ nm was chosen in order to reproduce the ionization energy of $I_P = V_{\text{ei}}(r \rightarrow 0) = -5.1$ eV for solid sodium.

The velocity Verlet algorithm [57] was applied to solve the classical equations of motion for electrons and ions numerically. This method takes into account the conservation of the total energy of the whole finite system, as long as there is no external potential. To follow the fast electron dynamics, time steps of 0.01 fs were taken to calculate the time evolution. Contrary to bulk MD simulations no periodic boundary conditions are applied.

Icosahedral arrangements of 55, 147, and 309 ions, see [28], were considered as initial configuration for the ion positions. For these nearly spherically, homogeneously distributed ions, the ion density typical for solid sodium is given by an ionic next neighbor distance of $d_0 = 0.212$ nm. In addition, randomly distributed ion configurations within a given sphere were considered for comparison and the number of ions was increased up to 1000 particles. Starting with a neutral cluster, the electrons have been positioned nearby the ions with small, randomly distributed deviations from the ion positions.

To simulate experiments where clusters are excited by short pulse lasers, MD simulations are performed under the influence of an electric field, assuming a Gaussian shape and pulse duration of about 100 fs. Due to the largely increased kinetic energy of the electrons, ionization processes occur. After the laser field is switched off, the ionization degree of the cluster is determined by the number of electrons found outside the cluster radius with positive total energy, so that they can escape from the cluster. Due to ion excitation on larger time scales, a slow expansion of the cluster begins.

Considering the single-time properties, it was found in [28] that already local thermodynamic equilibrium (LTE) is established within fs immediately after the electron heating. In particular, at each time step, the momentum distribution of electrons is well described by a Maxwell distribution, and the spatial density profile agrees with a Boltzmann distribution with respect to the average potential that is determined by the actual ion configuration and the self-consistent electronic mean field. The fact that electrons relax to LTE within a sub fs time interval, where the ion configuration remains nearly unchanged, enables us to separate the electron dynamics from the ion dynamics.

Subsequently, the dynamical properties of the electron subsystem can be calculated for a frozen ionic configuration thus referring to a specific time. This is considered as an adiabatic approximation to the true dynamical properties of the electron subsystem which have to take into account the slow change in the ion configuration. More rigorously, non-stationary time dependent correlation functions have to be treated for the full charged particle system.

Using the *restricted MD* (RMD) simulations scheme as introduced in [28], the ions are kept fixed acting as external trap potential. Starting from an initial state, the many-electron trajectory $\{\vec{r}_i(t), \vec{p}_i(t)\}$ is calculated, solving the

classical equations of motion of the electrons. From this, all further physical properties of the electron subsystem inside the cluster are determined. Within RMD simulations, we consider no temporal variation of the plasma parameters that are determined by the frozen ion distribution, and the degree of ionization. A long-time run can be performed in order to replace the ensemble average by a temporal average. This has been successfully done for the single-time properties such as the momentum distribution and the density profile, see [28] and will now be applied to the two-time correlation functions.

Using classical MD simulation techniques, the results are valid for non-degenerate plasmas. This restricts the temperature range to $T \geq 1$ eV where our simulations can be compared with realistic sodium clusters. Arbitrary values for the plasma parameter can be treated since we are not confined to the weak coupling limit as, e.g., in perturbation theory.

In our RMD calculations, we start from a homogeneous ion configuration (icosahedral or randomly distributed) inside the cluster at fixed ion density. A thermostat was used to heat the electrons. At each time step, a heating rate was calculated via comparison of the electron temperature T_e , calculated from the kinetic energy, and the intended final temperature T_{aim} . Hot electrons are emitted so that the cluster becomes ionized. Evaluating the trajectories of electrons, sufficient time of about 200 fs has to be allowed before a stationary ionization degree is established and thermal equilibrium is achieved, characterized by stationary distributions in position and momentum space.

Using the trajectories of all N_e electrons obtained from the RMD simulations scheme, the local current density $\vec{j}_e(\vec{r}, t)$ at position $\vec{r}$ was calculated for each time step t

$$\vec{j}_e(\vec{r}, t) = \lim_{\Delta V_{\vec{r}} \rightarrow 0} \frac{e}{m_e} \frac{1}{\Delta V_{\vec{r}}} \sum_{l=1}^{N_e} \vec{p}_l(t) \delta_{\Delta V_{\vec{r}}}(\vec{r}_l(t)), \quad (10)$$

which is the sum over all electron momenta $\vec{p}_l$ inside a small volume $\Delta V_{\vec{r}}$ at position $\vec{r}$, where $\delta_{\Delta V_{\vec{r}}}(\vec{r}_l(t)) = 1$, and $\delta_{\Delta V_{\vec{r}}}(\vec{r}_l(t)) = 0$ for electrons found outside $\Delta V_{\vec{r}}$. The size of the volume determines the spatial resolution of the local current density $\vec{j}_e(\vec{r}, t)$. However, it must be taken sufficiently large to reduce statistical fluctuations.

The bi-local correlation tensor of the spatially resolved current density is calculated according to Eq.(2) as

$$\left(\vec{j}_e(\vec{r}, 0); \vec{j}_e(\vec{r}', t) \right) = \frac{1}{N_\tau} \sum_{i=1}^{N_\tau} \vec{j}_e(\vec{r}, i \cdot \tau) \otimes \vec{j}_e(\vec{r}', i \cdot \tau + t), \quad (11)$$

with typical values of $N_\tau \sim 10^9$ and $\tau \sim 0.1$ fs. Its Laplace transformation reads

$$\langle \vec{j}_e(\vec{r}); \vec{j}_e(\vec{r}') \rangle_\omega = \int_0^\infty dt e^{i\omega t} \left(\vec{j}_e(\vec{r}, 0); \vec{j}_e(\vec{r}', t) \right). \quad (12)$$

In the following, we restrict ourselves to the diagonal components $\langle j_e^{\parallel}; j_e^{\parallel} \rangle_\omega$ of this tensor, where only parallel components of the current density vectors are correlated as already introduced in Sec. I. As it will be shown in the following sections, this bi-local current density correlation is important to understand the excitation modes of nano plasmas. The non-diagonal components of the bi-local correlation tensor are small in comparison to the diagonal components. Beside the bi-local current density correlation function considered here, the bi-local density fluctuation correlation $\langle \delta n(\vec{r}); \delta n(\vec{r}') \rangle_\omega$ as well as the bi-local force correlation $\langle \vec{F}(\vec{r}); \vec{F}(\vec{r}') \rangle_\omega$ are useful quantities in the context of optical properties. These correlations can be evaluated from the trajectory in a similar way and are related to the bi-local current density correlation, but will not be discussed here any further.

Because of the spherical symmetry of the cluster geometry during excitation and expansion, the volume is divided into cells $\Delta V_{\vec{r}}$ according to equidistant intervals of spherical coordinates, i.e. the distance to the center of the cluster r , the inclination angle θ as well as the azimuthal angle ϕ . The cluster radius R_i is given by the rms radius of ions according to $R_i^2 = 5/3 \langle r^2 \rangle$. Because the cluster is positively charged, all bound electrons will move inside this cluster radius. The cluster will be divided into a finite number of sections, which are numbered by a single counter $a = N_\phi N_\theta (k - 1) + N_\phi (j - 1) + i$ with three independent counters accordingly to the three coordinates: $i = 1..N_\phi$, $j = 1..N_\theta$ and $k = 1..N_r$. With respect to Eq.(11) the bi-local correlation matrix $D_{a,a'}(t) = \left(j_e^{(z)}(\vec{r}_a, 0); j_e^{(z)}(\vec{r}_{a'}, t) \right)$ for the spatially resolved cluster and its Laplace transform $D_{a,a'}(\omega) = \int_0^\infty dt e^{i\omega t} D_{a,a'}(t)$ have been calculated.

The total current density auto correlation function (ACF) can be calculated from the trajectories as well as from the frequency spectrum of the current density correlation matrix

$$\langle j_e^{\parallel}; j_e^{\parallel} \rangle_\omega = \frac{1}{V_{\text{cl}}^2} \sum_{a,a'} D_{a,a'}(\omega) \Delta V_{i,j,k} \Delta V_{i',j',k'}, \quad (13)$$

using the cluster volume $V_{cl} = \frac{4\pi}{3}R_i^3$ and the individual cell volumes

$$\begin{aligned}\Delta V_{i,j,k} &= \int_{2\pi(i-1)/N_\phi}^{2\pi i/N_\phi} d\phi \int_{\pi(j-1)/N_\theta}^{\pi j/N_\theta} d\theta \int_{R_i(k-1)/N_r}^{R_i k/N_r} dr r^2 \sin \theta \\ &= \frac{2\pi}{3N_\phi} \left(\frac{R_i}{N_r}\right)^3 (3k^2 - 3k + 1) \left(\cos \left[\frac{\pi}{N_\theta}(j-1) \right] - \cos \left[\frac{\pi}{N_\theta}j \right] \right).\end{aligned}\quad (14)$$

IV. FROM BI-LOCAL CORRELATION FUNCTION TO ELECTRON MODES

In the following, we discuss calculations for the current density ACF Eq.(13) and the bi-local current density correlation spectrum $D_{a,a'}(\omega)$. Exemplarily, we present results for the Na₃₀₉ cluster at electron temperature $T_e = 1$ eV, cluster charge $Z = 16$ and ionic density $n_i = 28.0 \cdot 10^{21} \text{ cm}^{-3}$. Calculations of other cluster sizes will be presented in the following sections. The real part of the current density ACF $\text{Re}\langle j_e^{\parallel}; j_e^{\parallel} \rangle_\omega$ is shown in Fig. 1. Three maxima are obtained. To investigate the origin of the maxima as collective excitations of the nano plasma, the bi-local current density correlation matrix was calculated as well.

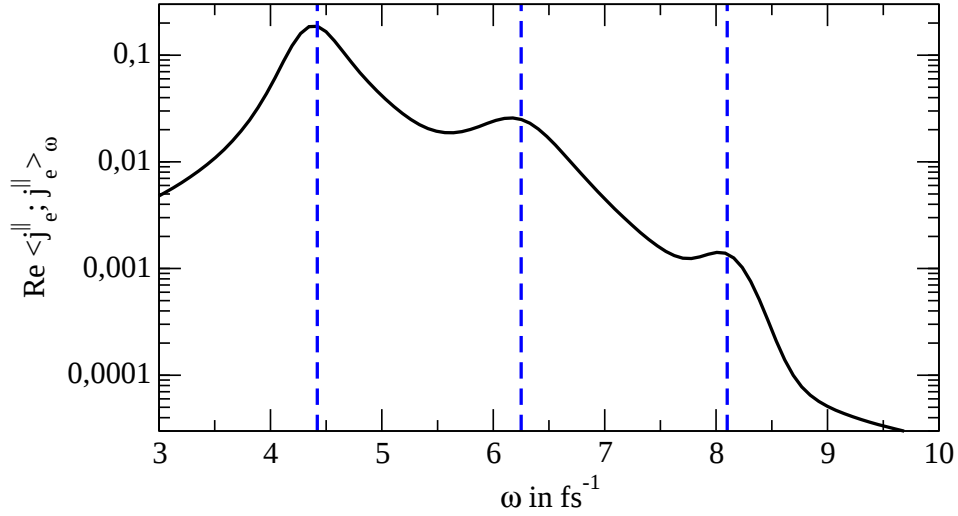


FIG. 1. Frequency spectrum of the real part of the current density ACF of a Na₃₀₉ cluster at electron temperature $T_e = 1$ eV, cluster charge $Z = 16$ and ionic density $n_i = 2.80 \cdot 10^{22} \text{ cm}^{-3}$.

The following spatial symmetries in the matrix $D_{a,a'}(\omega)$ were found

$$D_{i,j,k| i',j',k'}(\omega) = D_{i^*,j,k| j',k'}(\omega), \quad (15)$$

$$D_{i,j,k| i',j',k'}(\omega) = D_{i,N_\theta-j+1,k| i',N_\theta-j'+1,k'}(\omega), \quad (16)$$

$$D_{i,j,k| i',j',k'}(\omega) = D_{i,j,k'| i',j',k}(\omega), \quad (17)$$

where $i^* = |i - i'|$ or $i^* = N_\phi - |i - i'|$, if $|i - i'| > N_\phi/2$. In our case, the N_a^2 elements of the full matrix can be reduced to $N_{ind} = \frac{(N_r N_\theta + 1) N_r N_\theta}{4} (N_\phi + N_\phi \bmod 2)$ independent elements due to the symmetries Eq.(??), thus improving statistics via averaging equal elements.

Because of the different size of the section volume there are large variations in the statistical errors of the bi-local current density correlation matrix elements. The statistical errors are of comparable size in the bi local current correlation function

$$K_{a,a'}(\omega) = D_{a,a'}(\omega) \Delta V_{i,j,k} \Delta V_{i',j',k'}, \quad (18)$$

for which the following eigenproblem was solved,

$$\sum_{a'} \text{Re } K_{a,a'}(\omega) \Psi_{\mu,a'}(\omega) = K_\mu(\omega) \Psi_{\mu,a}(\omega). \quad (19)$$

Thus, the matrix is decomposed into eigenvectors $\Psi_{\mu,a}(\omega) = \Psi_{\mu,i,j,k}(\omega)$ as well as their eigenvalues $K_{\mu}(\omega)$ at each frequency. The eigenvectors represent the spatial structure of the mode ($\Psi_{\mu,i,j,k}(\omega) \rightarrow \Psi_{\mu}(\vec{r}; \omega)$). The orthonormality condition

$$\int d^3\vec{r} \Psi_{\mu}(\vec{r}, \omega) \Psi_{\mu'}(\vec{r}, \omega) = \delta_{\mu, \mu'}. \quad (20)$$

holds.

For two selected frequencies, the 10 strongest eigenvalues of the Na_{309} cluster are shown in Fig. 2 at $\omega = 4.42 \text{ fs}^{-1}$ (black) a resonance frequency was found, with one outstanding, leading eigenvalue. At off-resonant frequencies, i.e. $\omega = 5.50 \text{ fs}^{-1}$ (red), all eigenvalues are of the same order of magnitude.

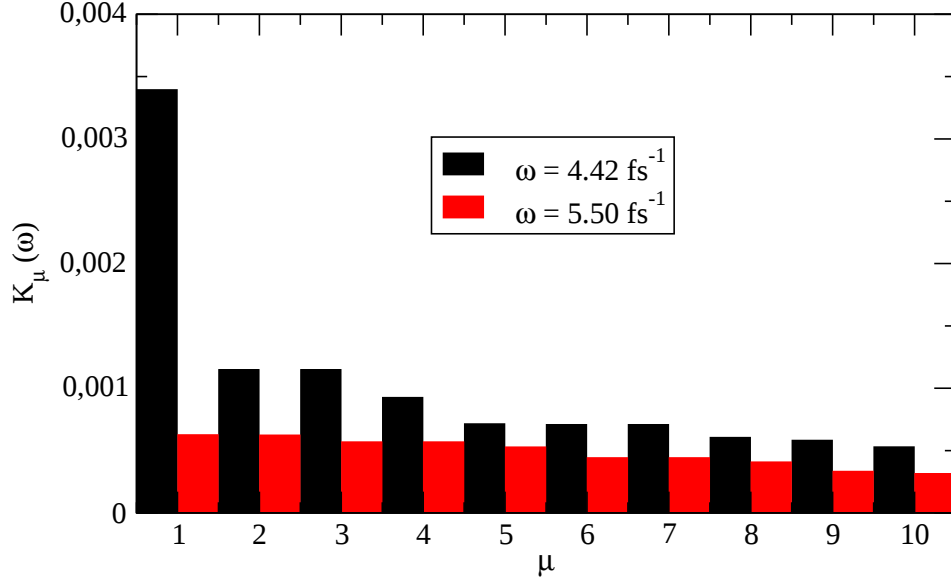


FIG. 2. Eigenvalues of the Na_{309} cluster sorted by size for the resonant case at $\omega = 4.42 \text{ fs}^{-1}$ (black) and a non-resonant case at $\omega = 5.50 \text{ fs}^{-1}$ (red), for parameters as in Fig. 1.

In Fig. 3 (left) 10 eigenvalues $K_{\mu}(\omega)$ of the Na_{309} cluster, as they result from Eq.(19), are shown in dependence of frequency. They are colored according to their strength and numbered ascending with descending strength. In the shown frequency range, modes $K_{\mu}(\omega)$ with well defined maxima are found. Spatial oscillation structure can be identified by analyzing the eigenvectors. In Fig. 3 (right), the spectra of eigenvalues are sorted in an alternative way, according to the same spatial oscillation structure of the eigenvector, which is obtained over the whole frequency range.

It is possible to separate resonance structures of different modes (distinguished by color). The black solid mode is the strongest. The resonance frequencies are also found in the total current density ACF (indicated via horizontal blue dashed lines). Resonances in the total current density ACF, shown in Fig. 1, are only possible in the case of non-zero total current, which is caused by a dipole-like oscillation. Therefore, resonances which are seen in the total current density ACF are oscillation modes with a dipole moment. After characterization of the resonance structures, the dipole-like resonances will be investigated in greater detail.

V. ANALYSIS OF THE COLLECTIVE MODES

The decomposition of the locally resolved current correlation matrix into eigenvalues $K_{\mu}(\omega)$, as shown in Fig. 3, gives a complex set of resonance structures. To analyze the spatial oscillation structure, a spherical Fourier decomposition of the eigenvectors into the spherical Bessel function $j_l(k_{n,l}r)$ and spherical harmonics $Y_{l,m}(\theta, \phi)$ was performed according to

$$\Psi_{\mu}(\vec{r}, \omega) = \sum_{n=1}^{N_n} \sum_{l=0}^{N_l} \sum_{m=-l}^l S_{n,l,m}(\omega) N_{n,l} j_l(k_{n,l}r) Y_{l,m}(\theta, \phi), \quad (21)$$

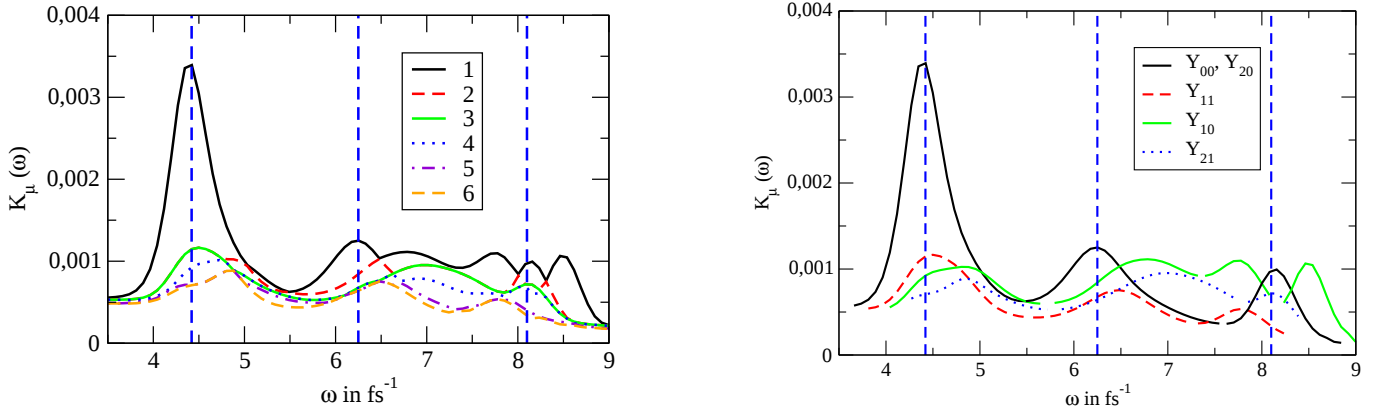


FIG. 3. Left: spectrum of the 10 highest eigenvalues $\text{Re}K_\mu(\omega)$ of the Na_{309} cluster for same parameters as in Fig. 1. Right: eigenvalues of the same cluster selected in terms of the corresponding spherical harmonics $Y_{l,m}(\theta, \phi)$.

where $S_{n,l,m}(\omega)$ is the spherical Fourier component with ordinal number n, l, m . The normalization factor $N_{n,l}$ as well as the wave number $k_{n,l}$ are chosen in the way that the eigenfunction has a root at the cluster surface.

In Fig. 3 (right) the four leading eigenvalue spectra were identified by the pair of the leading ordinal numbers l, m . The angular part of the eigenfunction to the spherical harmonics $Y_{l,m}(\theta, \phi)$. The dipole-like resonance structure is a mix of the same two spherical harmonics at all frequencies. As a consequence, one is able to point out similar properties of slightly different of eigenvectors $\Psi_\mu(\vec{r}, \omega)$ of the same resonance structure at different frequencies, represented by the pair of leading ordinal numbers l, m .

For example, the dipole-like mode, represented via solid black lines in Fig. 3 (right), with resonances at the same frequencies as in the total current density ACF (indicated via horizontal blue dashed lines), is characterized by the mix of the spherical harmonic functions $Y_{0,0}(\theta, \phi)$ and $Y_{2,0}(\theta, \phi)$. For the Na_{309} cluster, one can find three resonance frequencies. To draw a complete picture, the decomposition of the current matrix into eigenvectors and eigenvalues was done for a larger cluster consisting of 1000 ions. There, four pronounced dipole-like resonances were found. The spatial structures of the leading dipole-like mode of the current density $j(\vec{r}) \sim \frac{\Psi(\vec{r})}{\Delta V(\vec{r})}$ is shown for the Na_{1000} cluster in Fig. 4 at the resonance frequencies. The spatial mode structure of the current density $j_\mu(\vec{r}) \sim \frac{\Psi(\vec{r})}{V(\vec{r})}$ is shown.

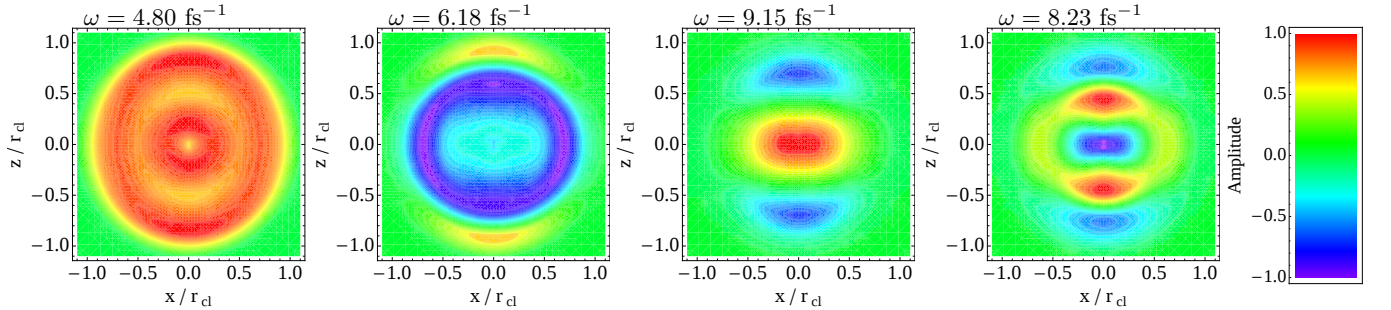


FIG. 4. Selected eigenvectors of the dipole-like mode in the Na_{1000} clusters for same parameters as in Fig. 1 but $Z = 19$.

At the resonance frequency $\omega_R = 4.80 \text{ fs}$, the electrons are oscillating with current densities $j_e(r)$ depending on the distance r , which is related to the density profile $n_e(r)$ of the electrons. As shown in Fig. 4 on the left hand side, all electrons of this mode are moving in the same direction and no nodes can be seen.

The third and fourth mode on the right hand side of Fig. 4 appear similar to a plane wave oscillation of electrons, but trapped inside the cluster. To identify a wave number of the plane wave oscillation, a Fourier decomposition in z -direction was done. A maximum at $k = 1.6 \text{ nm}^{-1}$ and $k = 4.7 \text{ nm}^{-1}$, respectively, appears, which belong to the wavelengths of the plane wave oscillations. The second resonance structure of Fig. 4, looks like a mix of the first and the third resonance structure. The plane wave oscillation with higher wavenumber was only found in the large cluster with 1000 ions. All other modes can be seen in smaller clusters as well.

We want to point out one further feature of the mode spectra in Fig. 3 (right). The dashed red line represents two resonance structures with exactly the same eigenvalues at all frequencies. The eigenvectors are orthogonal. Both eigenvectors are characterized by the same spherical harmonic function $Y_{1,1}(\theta, \phi)$ but have a phase shift in ϕ -direction:

$Y_{1,1}^{(1)}(\theta, \phi) = Y_{1,1}^{(2)}(\theta, \phi + \frac{\pi}{2})$. Further degenerations are obtained for lower eigenvalues.

All eigenvectors $\Psi_\mu(\vec{r}, \omega)$ are decomposed into a superposition of spherical Bessel functions $j_l(k_{n,l}r)$ with a set of ordinal numbers n . No leading ordinal number n was found, which characterizes the spatial resonance structure in r direction.

A. Resonance frequency of the rigid oscillation

The total current density ACF shown in Fig. 1 as well as the leading eigenvalue in Fig. 2 show a strong resonance at the frequency $\omega_R \approx 4.42 \text{ fs}^{-1}$. This resonance belongs to the dipole-like mode with the eigenvector shown in Fig. 4 on the left hand side. We will now analyze this collective excitation mode in terms of a rigid oscillation.

The electrons with density profile $n_e(\vec{r})$ are assumed to move nearly rigidly in the external potential $V_{\text{ext,ei}}(\vec{r})$ due to the fixed ions. The potential energy of the electrons due to a small shift with respect to the ions reads

$$U_e(z) = \int d^3\vec{r} n_e(\vec{r}) V_{\text{ext,ei}}(\vec{r} - z\vec{e}_z). \quad (22)$$

The change of the potential energy $U_e(z)$ in z direction is due to the restoring force on the electron profile. In harmonic approximation of the equation of motion, the resonance frequency is identified as

$$m_e N_e \omega_R^2 = - \left. \frac{\partial^2 U_e(z)}{\partial z^2} \right|_{z=0}. \quad (23)$$

For small rigid shifts $z \rightarrow 0$, assuming radially dependent electron density profiles and external potentials in Eq.(22) the angular dependence of the potential energy calculation can be executed. The resonance frequency Eq.(23) is given according to

$$\omega_R^2 = \frac{4\pi}{3m_e N_e} \int_0^\infty dr n_e(r) r^2 \left(V''_{\text{ext,ei}}(r) + 2 \frac{V'_{\text{ext,ei}}(r)}{r} \right). \quad (24)$$

As a first example for a density profile, we assume a homogeneously charged ion sphere with radius $R_i = (3N_i/(4\pi n_i))^{1/3}$ and an electron sphere with radius $R_e = (3N_e/(4\pi n_e))^{1/3}$ just on the density. The densities of the electron and ion spheres is equal ($n_e = n_i$). Therefore, the difference of ion and electron radius is determined by the cluster charge, basically the difference of the simulated electron number N_e and ion number N_i . Thus, in the case of positive charged clusters, as discussed here, the electron sphere radius is smaller than the ion radius ($R_e < R_i$). The error function potential Eq.(9) was taken as electron-ion-interaction potential for the calculation of the resonance frequency, as it was used for the MD simulation as well. The resonance frequency then reads

$$\begin{aligned} \omega_R^2(R_i, R_e) = \omega_{\text{Mie}}^2 & \left[\frac{R_i^3 + R_e^3}{2R_e^3} \text{erf}\left(\frac{R_i + R_e}{\lambda}\right) - \frac{R_i^3 - R_e^3}{2R_e^3} \text{erf}\left(\frac{R_i - R_e}{\lambda}\right) + \right. \\ & \left. \frac{e^{-\frac{R_i^2 + R_e^2}{\lambda^2}}}{\sqrt{\pi} R_e^3} \left(\left[\frac{\lambda^3}{2} - \lambda(R_i^2 + R_e^2) \right] \sinh\left(\frac{2R_i R_e}{\lambda^2}\right) - \lambda R_i R_e \cosh\left(\frac{2R_i R_e}{\lambda^2}\right) \right) \right]. \end{aligned} \quad (25)$$

In the limit of large clusters with high number of ions the resonance frequency equals the Mie frequency $\lim_{R_i \rightarrow \infty} \omega_R(R_i) = \omega_{\text{Mie}}$. In this case the sphere radii have nearly the same size ($R_e \rightarrow R_i$) and the system is nearly neutral. The limit for very small cluster, till down to just one atom, depends on the pseudopotential. In our case, the resonance frequency $\lim_{N_i \rightarrow 1} \omega_R(N_i) = \frac{e^2}{4\pi\epsilon_0} \frac{4}{3\sqrt{\pi}\lambda^3 m_e}$ is due to the oscillation of a single electron in the ionic error-function pseudo-potential Eq.(9).

In Fig. 5 (left) the dependence of the resonance frequency ω_R of the dipole-like mode is shown in dependence on the size of the ion sphere. Empty circles represent results from MD simulations for a Na_{55} cluster at $n_i = 2.15 \cdot 10^{22} \text{ cm}^{-3}$ as well as for the Na_{309} cluster and Na_{1000} cluster at $n_i = 2.80 \cdot 10^{22} \text{ cm}^{-3}$. The cluster size dependent resonance frequency was calculated using Eq.(25) for ion densities of $n_i = 2.15 \cdot 10^{21} \text{ cm}^{-3}$ (solid red line) and $n_i = 2.80 \cdot 10^{21} \text{ cm}^{-3}$ (solid black line). The limit of both cases for large clusters, the Mie frequency $\omega_{\text{Mie}}^2 = \frac{e^2 n_i}{3\epsilon_0 m_e}$, is given as well as dotted lines colored accordingly.

Additionally, the electron density profile $n_e(r)$ was deducted from MD simulations for all cluster sizes and used to derive the resonance frequency ω_R solving Eq.(24) numerically. As a result, one is able to identify the resonance frequency of the dipole-like mode with a deviation to the direct simulation results of less than 5%. Using homogeneously a charged ion and electron sphere leads to reasonable agreement in the limits of large clusters as well as for small clusters. However, the spatial structure of the density profile more accurate calculations of the resonance frequency in the intermediate cluster size regime.

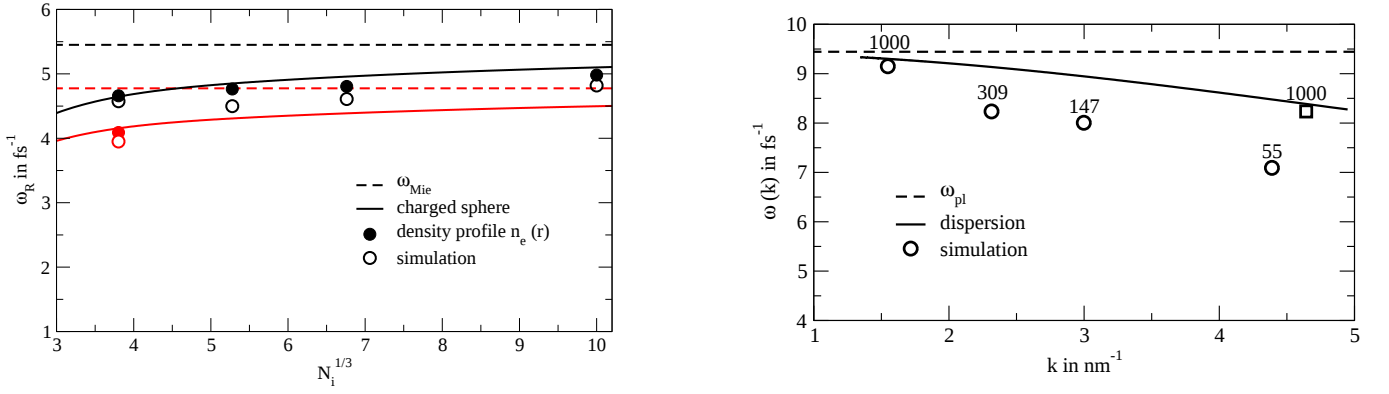


FIG. 5. Left: Cluster size dependent resonance frequency $\omega_R(R_i)$. Simulation results (empty circles) and analytical calculations (solid lines) using Eq.(25) are shown for $n_i = 2.15 \cdot 10^{22} \text{ cm}^{-3}$ (red) and $n_i = 2.80 \cdot 10^{22} \text{ cm}^{-3}$ (black). The limit for large clusters is given as well (dashed line). Numerical calculations using Eq.(24) are presented (black and red dots). Right: Dispersion Eq.(32) of a plane wave in a homogeneously charged sphere (solid lines) for $n_e = 2.80 \cdot 10^{22} \text{ cm}^{-3}$ as well as simulation results (empty symbols).

B. Dispersion of the plane wave mode

While the Mie-like resonance, discussed in the previous subsection is almost spherically symmetric, we obtain an increasing plane wave character of the dipole-like mode with increasing frequency. The third resonance frequency of the total current density ACF at $\omega_R = 8.14 \text{ fs}^{-1}$, see Fig. 1, is mainly caused by a plane wave like eigenvector as shown in Fig. 4 (right). Here, oscillations of electrons in opposite directions must be taken into account for the analytical calculation of the resonance frequency. The electron motion is treated as a hydrodynamical liquid using the Euler equation

$$\frac{\partial \vec{j}(\vec{r}, t)}{\partial t} = -\text{div} [\vec{j}(\vec{r}, t) \otimes \vec{v}(\vec{r}, t)] - \frac{1}{m_e} \text{grad } p(\vec{r}, t) - \frac{n_e(\vec{r}, t)}{m_e} \text{grad } V_{\text{ext}}(\vec{r}, t), \quad (26)$$

where $\vec{j}(\vec{r}, t) = n_e(\vec{r}, t) \vec{v}(\vec{r}, t)$ is the spatially resolved current density of the electrons, $p(\vec{r}, t)$ is the pressure of the electron gas and $V_{\text{ext}} = V_{\text{ext}, \text{ei}} + V_{\text{ext}, \text{ee}}$ is the external potential, composed of contributions from the electrons and ions. First, one is able to linearize the Euler equation due to a small perturbation in z -direction restricted to longitudinal effects

Using the following ansatz

$$j_z(\vec{r}, t) = \delta j \vec{e}_z e^{i(kz - \omega t)}, \quad (27)$$

$$v_z(\vec{r}, t) = \delta v \vec{e}_z e^{i(kz - \omega t)}, \quad (28)$$

$$n_e(\vec{r}, t) = n_{e,0}(r) + \delta n_e e^{i(kz - \omega t)}, \quad (29)$$

$$V_{\text{ext}}(\vec{r}, t) = V_{\text{ext},0} + \delta V_{\text{ext}}(\vec{r}) e^{i(kz - \omega t)}, \quad (30)$$

for a small perturbation in z -direction restricting ourselves to longitudinal effects, one is able to linearize the Euler equation. The system is assumed to be in LTE, described by the quantities $n_{e,0}(r)$, $\vec{j}_0(\vec{r}) = 0$, $\vec{v}_0(\vec{r}) = 0$ as well as $V_{\text{ext},0}(r)$. One has to consider now electrons moving in an external field of ions and electrons to construct the external potential

$$V_{\text{ext}}(\vec{r}, t) = \int d^3 \vec{r}_1 \left(n_i(r_1) - \frac{n_{e,0}(r_1)}{2} \right) V_{e,i}(\vec{r}_1 - \vec{r}) + \frac{1}{2} \int d^3 \vec{r}_1 \delta n_e(r_1, t) V_{e,e}(\vec{r}_1 - \vec{r}), \\ V_{\text{ext}}(\vec{r}, t) = V_{\text{ext},0}(r) + \delta V_{\text{ext}}(\vec{r}, t). \quad (31)$$

Finally, the external potential has a equilibrium part and a perturbative part $\delta V_{\text{ext}}(\vec{r}, t)$, which is mainly dependent on the linear density perturbation $\delta n_e(\vec{r}, t)$.

Assuming Boltzmann distribution to express the gas pressure of the electrons $p(\vec{r}, t)$ via the electron density and using the equation of continuity, one is able to express the Euler equation in terms of linear perturbations of the density. Thus, the equilibrium part of the external potential compensates the pressure term on the right hand side of Eq.(26). Because we are interested in linear perturbations of the Euler equation, only the third term on the right

hand side of Eq.(26) remains, which is connected to the external potential. Finally, leading all terms of the Euler equation Eq.(26) back to a linear density fluctuation $\delta n_e(\vec{r}, t)$, one ends up with

$$\omega^2(k) = \frac{\omega_{\text{pl}}}{4} e^{-\frac{k}{4}(k\lambda^2 + 4iR_e)} \left(i e^{ikR_e} \left[\text{erfi} \left(\frac{k\lambda^2 - 2ikR_e}{2\lambda} \right) - \text{erfi} \left(\frac{k\lambda^2 + 2ikR_e}{2\lambda} \right) \right] - e^{\frac{k^2\lambda^2}{4}} [1 + e^{2ikR_e}] \text{erf} \left(\frac{R_e}{\lambda} \right) \right). \quad (32)$$

This relation leads to real solutions for the resonance frequencies only for standing waves with $k_n = n\pi/R_e$ and scales with the plasma frequency ω_{pl} .

From the eigenvector of the plane wave mode, one can derive the wave number $k = \pi/R_e$, which corresponds to $n = 1$. This means the dispersion of the plane wave mode is determined by the radius of the electron cloud. Results for this case are shown in Fig. 5 (right) for different cluster sizes and are compared with simulation data. For the cluster with 1000 ions a plane wave mode with $k = 3\pi/R_e$ and $n = 3$, respectively, was found as well. The simulation data for the Na₁₀₀₀ cluster fit the dispersion Eq.(32) as well. Deviations of the plane wave resonance for smaller clusters are related to the radial dependence of the electron density profile.

VI. CONCLUSION

We have investigated collective excitation modes of a nano plasma in highly excited metal clusters. The collective excitation of electrons inside the cluster are obtained from bi-local current density correlation functions by solving the eigenvalue problem of the current density correlation matrix. Therefore, the local current density $\vec{j}(\vec{r}, t)$ for excited clusters of 55 up to 1000 ions with densities of $n_i = 2.15 \cdot 10^{22} \text{ cm}^{-3}$ as well as $2.80 \cdot 10^{22} \text{ cm}^{-3}$ and temperatures of $T_e = 1 \text{ eV}$ has been calculated using RMD simulations. Pseudo-potentials of sodium were used to calculate the electron dynamics without consideration of degeneration effects. This limits us to temperatures of a few $T_e \geq 1 \text{ eV}$. For the analysis of electron dynamics at temperatures less than $T_e = 1 \text{ eV}$, the inclusion of quantum effects for the calculation of the local current density $\vec{j}(\vec{r}, t)$ of cluster electrons is an open question at this point. It is useful to go beyond classical description to discuss for example cold, non-excited clusters.

The spectrum of a dipole-like mode was investigated. The leading mode more in detail. Using analytical calculations, it was possible to relate the position of resonance modes in the frequency domain to their spatial mode structure. The width of mode resonances and the role of collision-less damping effects as well as the collision frequency needs to be investigated in the future. The systematic change of the collision frequency with cluster size up to the bulk limit remains an interesting field. A first step was done here, presenting the cluster size dependence of resonance frequencies. The experimental verification of modes beyond the Mie resonance are desirable. Collective effects of electron motion have to be taken into account when analyzing ultraviolet (UPS) or x-ray photoelectron spectroscopy (XPS) experiments, as [22].

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- [1] A. McPherson, K. Boyer, and C. K. Rhodes; *J. Phys. B* **27**, L637 (1994).
 - [2] T. Ditmire, J. W. G. Tisch, E. Springate, M. B. Mason, N. Hay, R. A. Smith, J. Marangos, and M. H. R. Hutchinson; *Nature* **386**, 54 (1997).
 - [3] M. Lezius, S. Dobosz, D. Normand, and M. Schmidt; *Phys. Rev. Lett.* **80**, 261 (1998).
 - [4] L. Köller, M. Schumacher, J. Köhn, S. Teuber, J. Tiggesbäumker, and K.-H. Meiwes-Broer; *Phys. Rev. Lett.* **82**, 3783 (1999).
 - [5] R. Schlipper, R. Kusche, B. v. Issendorff, and H. Haberland; *Phys. Rev. Lett.* **80**, 1194 (1998).
 - [6] V. P. Krainov and M. B. Smirnov; *Physics Uspekhi* **43**, 901 (2000).
 - [7] P.-G. Reinhard, and E. Suraud; *Introduction to Cluster Dynamics*, Wiley, New York, 2003.
 - [8] U. Saalmann, Ch. Siedschlag and J. M. Rost; *J. Phys. B* **39**, R39 (2006).
 - [9] T. Döppner, T. Diederich, A. Przystawik, N. X. Truong, T. Fennel, J. Tiggesbäumker, and K. - H. Meiwes-Broer; *Phys. Chem.* **9**, 4639 (2007).
 - [10] T. Ditmire, R. A. Smith, T. W. G. Tisch, and M. H. R. Hutchinson; *Phys. Rev. Lett.* **78**, 3121 (1997).

- [11] A. McPherson, B. D. Thompson, A. B. Borisov, K. Boyer, C. K. Rhodes; *Nature* **370**, 631 (1994).
- [12] S. Dobosz, M. Lezius, M. Schmidt, P. Meynadier, M. Perdrix, D. Normand, J.-P. Rozet, and D. Vernhet; *Phys. Rev. A* **56**, R2526 (1997).
- [13] T. Ditmire, T. Donnelly, R. W. Falcone, and M. D. Penz; *Phys. Rev. Lett.* **75**, 3122 (1995).
- [14] Y. L. Shao, T. Ditmire, J. W. G. Tisch, E. Springate, J. P. Marangos, and M. H. R. Hutchinson; *Phys. Rev. Lett.* **77**, 3343 (1996).
- [15] T. Ditmire, E. Springate, J. W. G. Tisch, Y. L. Shao, M. B. Mason, N. Hay, J. P. Marangos, and M. H. R. Hutchinson; *Phys. Rev. A* **57**, 369 (1998).
- [16] C. Deiss, N. Rohringer, and J. Burgdörfer; *Phys. Rev. Lett.* **96**, 013203 (2006).
- [17] S. Micheau, C. Bonte, F. Dorchies, C. Fourment, M. Harmand, H. Jouin, O. Peyrusse, B. Pons, and J. J. Santos; *H. En. Dens. Phys.* **3**, 191 (2007).
- [18] T. Fennel, T. Döppner, J. Passig, C. Schaal, J. Tiggesbäumker, and K.-H. Meiwes-Broer; *Phys. Rev. Lett.* **98**, 143401 (2007).
- [19] C. Xia, C. Yin, and V. V. Kresin; *Phys. Rev. Lett.* **102**, 156802 (2009).
- [20] S. Hüfner; *Photoelectron Spectroscopy*; Springer-Verlag, Berlin Heidelberg, 1995.
- [21] V. Senz, T. Fischer, P. Oelšner, J. Tiggesbäumker, J. Stanzel, C. Bostedt, H. Thomas, M. Schöffler, L. Foucar, M. Martins, J. Neville, M. Neeb, T. Möller, W. Wurth, E. Rühl, R. Dörner, H. Schmidt-Böcking, W. Eberhardt, G. Ganteför, R. Teuch, P. Radcliffe, and K.-H. Meiwes-Broer; *Phys. Rev. Lett.* **102**, 138303 (2009).
- [22] T. Andersson, C. Zhang, A. Rosso, I. Bradeanu, S. Legendre, S. E. Canton, M. Tchalyguine, G. Öhrwall, S. L. Sorensen, S. Svensson, N. Martensson, and O. Björneholm; *J. Chem. Phys.* **134**, 094511 (2011).
- [23] T. Ditmire, J. Zweiback, V. P. Yanovsky, T. E. Cowan, G. Hays, and K. B. Wharton; *Nature* **398**, 489 (1999).
- [24] G. Grillon, P. Balcou, J.-P. Chambaret, D. Hulin, J. Martino, S. Moustazis, L. Notebaert, M. Pittman, Th. Pussieux, A. Rousse, J.-Ph. Rousseau, S. Sebban, O. Sublemontier, and M. Schmidt; *Phys. Rev. Lett.* **89**, 065005 (2002).
- [25] K. W. Madison, P. K. Patel, M. Allen, D. Price, R. Fitzpatrick, and T. Ditmire; *Phys. Rev. A* **70**, 053201 (2004).
- [26] K. Höfflich, U. Gosele, and S. Christiansen; *Phys. Rev. Lett.* **103**, 087404 (2011).
- [27] N. Verellen, Y. Sonnefraud, H. Sobhani, F. Hao, V. V. Moshchalkov, P. V. Dorpe, P. Nordlander, and S. Maier; *Nano Lett.* **9**, 1663 (2009).
- [28] T. Raitza, H. Reinholz, G. Röpke, I. Morozov, and E. Suraud; *Contrib. Plasma Phys.* **49**, 498 (2009).
- [29] T. Raitza, H. Reinholz, G. Röpke, and I. Morozov; *J. Phys. A* **42**, 214048 (2009).
- [30] T. Raitza, H. Reinholz, and G. Röpke; *Int. J. of Mod. Phys. B* **24**, 4961 (2010).
- [31] T. Raitza; *PhD Thesis*, Rostock, 2011.
- [32] P.-G. Reinhard, O. Genzken, and M. Brack; *Ann. Phys.* **5**, 576 (1996).
- [33] F. Greschik and H.-J. Kull; *Laser and Particle Beams* **22**, 137 (2004).
- [34] L. Arndt; *PhD Thesis*, Köln, 2006.
- [35] P.-G. Reinhard, Lu Guo, and J. A. Maruhn; *Eur. Phys. J. A* **32**, 19 (2007).
- [36] F. Calvayrac, P.-G. Reinhard, E. Suraud, and C. A. Ullrich; *Phys. Rep.* **337**, 493 (2000).
- [37] J. Köhn, R. Redmer, K.-H. Meiwes-Broer, and T. Fennel; *Phys. Rev. A* **77**, 033202 (2008).
- [38] U. Saalman, I. Georgescu, and J. M. Rost; *New J. Phys.* **10**, 25014 (2008).
- [39] P. Hilse, M. Schlages, T. Bornath, and D. Kremp; *Phys. Rev. E* **71**, 56408 (2005).
- [40] W. Ekardt; *Phys. Rev. B* **29**, 1558 (1984).
- [41] S. Kümmel, M. Brack, and P.-G. Reinhard; *Phys. Rev. B* **62**, 7602 (2000).
- [42] M. Brack, P. Winkler, and M. V. N. Murthy; *Int. J. of Mod. Phys. E* **17**, 138 (2008).
- [43] S. A. Chin, and E. Krotscheck; *Phys. Rev. E* **72**, 036705, (2005).
- [44] L. Ramunno, C. Jungreuthmayer, H. Reinholz, and T. Brabec; *J. Phys. B* **39**, 4923 (2006).
- [45] H. Reinholz, T. Raitza, and G. Röpke; *Int. J. Mod. Phys. B* **21**, 2460 (2007).
- [46] H. Reinholz, T. Raitza, G. Röpke, and I. Morozov; *Int. J. Mod. Phys. B* **22**, 4627 (2008).
- [47] D. Zubarev, V. Morozov, and G. Röpke; *Statistical Mechanics of Nonequilibrium Processes II*, Akademie Verlag, Berlin, 1997.
- [48] H. Reinholz; *Ann. Phys. Fr.* **30**, N° 4 - 5 (2006).
- [49] H. Reinholz, R. Redmer, G. Röpke, and A. Wierling; *Phys. Rev. E* **62**, 5648 (2000).
- [50] I. Morozov, H. Reinholz, G. Röpke, A. Wierling, and G. Zwicknagel; *Phys. Rev. E* **71**, 066408 (2005).
- [51] D. Bohm and E. P. Gross *Phys. Rev.* **75**, 1864 (1949).
- [52] W.-D. Kraeft, D. Kremp, W. Ebeling, and G. Röpke; *Quantum Statistics of Charged Particle Systems*, Akademie-Verlag, Berlin, 1986.
- [53] R. Thiele, T. Bornath, C. Fortmann, A. Höll, R. Redmer, H. Reinholz, G. Röpke, A. Wierling, S. H. Glenzer, G. Gregori; *Phys. Rev. E* **78**, 026411 (2008).
- [54] H. Reinholz, I. Morozov, G. Röpke, and T. Millat; *Phys. Rev. E* **69**, 066412 (2004).
- [55] C. Fortmann; *Phys. Rev. E* **79**, 016404 (2009).
- [56] M. Belkacem, F. Megi, P.-G. Reinhard, E. Suraud, and G. Zwicknagel; *Eur. Phys. J. D* **40**, 247 (2006).
- [57] L. Verlet; *Phys. Rev.* **159**, 98 (1967).